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**1 Mar 96 - 28 Feb 97**

**for**

***NATO ASI on  
Plasma Processing  
of Semiconductors***

**AFOSR Grant F49620-96-1-0050**

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**Submitted to  
Dr Robert J. Barker  
AFOSR/NE**

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## INTRODUCTION TO PLASMA ETCHING

T. D. MANTEI

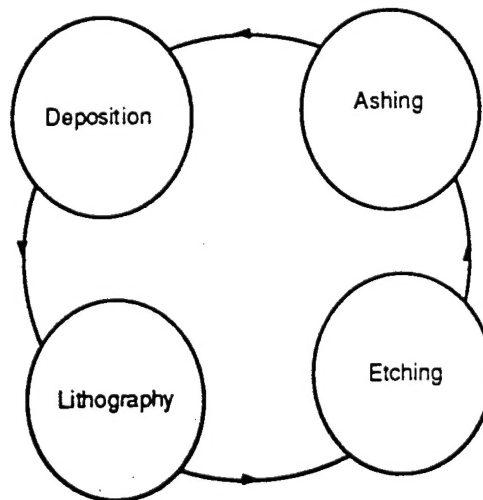
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### 1. Introduction

Plasma etching has become a crucial process step for the microelectronics industry, as computer logic and memory circuits require increasingly precise fabrication of fine-scale patterns in semiconductors, metals, and insulators. Plasma etching generally involves the dissociation and ionization of a neutral precursor gas to form reactive neutral fragments and charged ions and electrons. The substrate to be etched is placed in contact with this mixture, and etching proceeds through the synergistic interaction of the substrate, corrosive neutral species, and directionally impinging plasma ions.

#### 1.1 THE PROCESS CYCLE

A typical microelectronic fabrication sequence usually comprises four main process steps: deposition, patterning, etching, and ashing (Fig. 1).



*Figure 1. Schematic process cycle.*

In the deposition step, a metal, semiconductor, or dielectric film is applied to the wafer, e.g. gate oxide, field oxide, gate polysilicon, contact or interconnect metal, and so on. The deposited film is then lithographically patterned or masked with a protective

## PLASMA CHEMISTRY, BASIC PROCESSES, AND PECVD

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### 1. What is Plasma Chemistry?

Plasma chemistry deals with chemical reactions and modifications which are mediated by partially ionized gases. These plasmas span an astounding range of parameter space, up to 20 orders of magnitude in some key variables such as electron density.

A partially ionized gas contains particles with net free charge. When all particles comprising a gas are charged, the gas is said to be fully ionized. Fully ionized media are common in the galaxy, but find less use in applications. The term plasma, as distinguished from ionized gas, denotes a medium with substantially equal concentrations of positive and negative charges. Positive and negative charge is held together by electrostatic force. This force maintains large scale neutrality, when an ionized gas extends over a distance larger than a Debye length,  $\lambda_D$ . The Debye length scale is determined by the competition between random thermal diffusion moving particles away from each other and electrostatic attraction which draws together particles of opposite charge.

In plasmas used for chemical and device processing ("processing plasmas"), much of the free negative charge is carried by electrons. Electrons are lighter than other particles by a factor of 1000 to 10,000, so they move much faster and have very high diffusivity. Another "property" of the fast-moving electrons is that they give up very little of their energy in a non-reactive (elastic) collision with gas molecules. This is so because of the electron to gas mass disparity— the maximum energy which can be transferred from one particle to another in elastic ("billiard-ball") collision is only  $2m/M$ , where  $m$  is the mass of the lighter collision partner (electrons) and  $M$  is the mass of the heavier one.

In low pressure plasmas the random "thermal" electron energy is usually many times higher than the neutral gas. A perspective is to think of the "hot" electron gas with temperature  $T_e$ , as being somewhat independent of the cool neutral gas at temperature  $T_g$  (weakly coupled). This comes about because nearly all electrical excitation power is given to the electrons, whereas only a small fraction of an electron's energy is imparted to neutral gas molecules upon each collision. These counteracting energy flows force electronic energy to increase up to the point where the fraction, although small, is a fraction of a large electron energy— on the order of electron volts. The energy lost can

## THE ROLE OF IONS IN REACTIVE ION ETCHING WITH LOW DENSITY PLASMAS

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### 1. Introduction

Several studies of plasma-assisted etching were reported in the mid-1970s which demonstrated the importance of energetic ion bombardment [1-3]. In this work the terms *chemical sputtering* [2] and *reactive ion etching (RIE)* [3] were introduced. Subsequently, directed beam studies [4] showed more clearly the synergism between energetic ions and chemically reactive species incident on surfaces on which the reactive species can react with the surface to form volatile products.

This ion-assisted gas-surface chemistry is probably the most important of the phenomena resulting from energetic ion bombardment of solids in the presence of a reactive gas which reacts with the solid to form a volatile product. However, this phenomenon is not well understood at the microscopic level even in those gas-solid systems which have been investigated quite thoroughly (e.g., Si-F and Si-Cl).

Other phenomena which can influence the behavior of solids subjected to energetic ion bombardment and reactive gas fluxes simultaneously are: 1. Ion-induced mixing or diffusion of reactive species below the top surface of the substrate; 2. Physical sputtering; 3. Ion-induced damage (emphasizing the effect of this damage on the chemical reactivity of the surface); 4. Ions as a source of chemical reactants. In low density plasmas, the flux of ions is so much smaller than the flux of neutrals that the chemical contribution of the ion flux is usually insignificant. For example a typical ion current density in low density plasmas might be  $0.5 \text{ ma/cm}^2$  which corresponds to a particle flux of about  $3 \times 10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$ . However a typical pressure of neutral atoms or radicals might be a few tens of millitorr. For Cl atoms at 20 millitorr, the flux is approximately  $6 \times 10^{18} \text{ cm}^{-2} \text{ sec}^{-1}$  which is 2000 times the ion flux. However in high density plasmas the chemical importance of the ion flux is much larger and this will be discussed elsewhere in this volume [5].



## **SiO<sub>2</sub> ETCHING IN HIGH-DENSITY PLASMAS: DIFFERENCES WITH LOW-DENSITY PLASMAS**

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### **1. Introduction**

Silicon dioxide (SiO<sub>2</sub>) is the most important insulator employed in silicon integrated circuit (IC) technology. It is used as the material of choice to electrically isolate the conductive portions of devices or circuits from each other, e.g. as the gate insulator of field effect transistors, field oxide or trench refill material when isolating individual devices, and as interlevel dielectric which isolates the metallic interconnections between individual devices from each other.[1] State-of-the-art ICs employ up to 5 metal wiring levels at this time, and the use of up to 8 levels of metal is projected within several years. The wiring is imbedded in an equal number of deposited and subsequently patterned SiO<sub>2</sub> films.

These uses of SiO<sub>2</sub> require frequent patterning of SiO<sub>2</sub> during IC manufacturing. At this time this is accomplished using reactive ion etching (RIE). Silicon dioxide patterning by means of a plasma process in IC manufacturing has to fulfill a number of constraints. The removal of SiO<sub>2</sub> has to be accomplished at a practical rate, while maintaining vertical etch profiles in features of differing widths, and then stopping on various, chemically similar underlayers. At the same time, photomasks are growing thinner and less resistant to the etch process as the lateral dimensions defined by lithography are reduced, which requires improved etch selectivity to the mask. Table 1, from the work of Cook et al.[2], summarizes important requirements on a silicon dioxide plasma etching process for use in manufacturing of the 0.35  $\mu\text{m}$  generation.

Low pressure high-density plasma sources have become the standard for patterning conductors, e.g. poly-silicon and aluminum films, because they enable (1) higher etching rates (ER), (2) improved etch selectivity and surface damage control and (3) reduced RIE Lag (the slow-down of the etch rate as a function of feature size or aspect ratio) relative to traditional capacitively coupled RIE. The shift from low-density RIE technology to high-density plasma technology has as yet not been successful for silicon dioxide etching in IC manufacturing. This is principally due to the difficulty in adapting the fluorocarbon silicon dioxide etching chemistry that is required to obtain adequate SiO<sub>2</sub>/photoresist and SiO<sub>2</sub>/Si etch selectivity to the high-density plasma environment.[3,4]

In this article a review of silicon dioxide patterning in low pressure high-density plasmas is presented. Before we describe this topic, we present a brief review of SiO<sub>2</sub> patterning in conventional rf plasmas.

## Introduction to Plasma Enhanced Chemical Vapor Deposition

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### 0. Overview

Chemical vapor deposition (CVD) is a process in which gaseous species react on solid substrates to form solid, nonvolatile films. The energy needed to activate the chemical reactions can be provided in several different forms; *e.g.*, thermal, photon, or plasma. When a plasma or (to be more accurate) a glow discharge is used to provide at least some of the energy needed in a CVD process the process is called plasma enhanced CVD (PECVD). This Chapter begins with a brief, 'big picture' view of PECVD processes and applications relevant to semiconductor device manufacturing. More details can be found in several texts which cover this topic more extensively [1-4].

Even though PECVD has been used for many years, fundamental understanding of the processes is limited. As our understanding and information base have improved, models of increasing complexity have been developed and used to relate process parameters to process performance; *i.e.*, deposition rate and conformality. We present a case study of the model development and verification for plasma enhanced deposition of silicon dioxide from tetraethylorthosilicate (TEOS) to highlight timely, engineering model development and the benefits of increasing model complexity only as necessary. This case study serves as a useful example of how combined modeling and experimental work can lead to tools which can be used to guide process design and selection. The tools have been adopted by industrial colleagues, who often cannot wait until more detailed modeling work has been completed to make decisions. In addition, the first and second generation models serve as 'stepping stones' before jumping into the daunting task of understanding more complete plasma models, which are discussed in other chapters. This on-going case study is presented in roughly the chronological order in which the work was done.

### 1. PECVD in Semiconductor Device Manufacturing

In semiconductor device manufacturing PECVD processes are used to deposit dielectric films. PECVD processes for depositing metal and epitaxial layers have been developed in

## Topography Evolution During Semiconductor Processing

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### 1. Introduction

Many processes performed during the fabrication of microelectronic circuits result in changes in the shape and/or composition of the wafer surface. This is particularly true of deposition, etch and 'planarization' steps; *e.g.*, thin film flow (or 'reflow') and chemical mechanical polishing (CMP) steps. It is well known that differences in the surface shape and/or composition (referred to as 'topography' in this chapter) at one or more critical steps in the process flow can result in significant differences in circuit yield and performance; particularly for advanced device structures. The importance of topography relevant steps in determining device and circuit performance explains the widespread interest in simulations of the time evolution of topography during deposition, etch and planarization processes.

A 'topography simulator', for the purposes of this chapter, 1) predicts (or at least specifies) the surface velocities (*e.g.*, growth or etch rates) over an entire surface, at any time, and 2) moves the surface, using these velocities to predict the time evolution of the topography. One long term goal in the field of microelectronics relevant technology computer aided design (TCAD) is the ability to predict device and circuit performance based on the structures predicted using process simulators, including topography simulators; *i.e.*, to develop a 'virtual fab' in which products can be developed more rapidly and cost effectively than using largely empirical development, as is currently done. The simulation models in these virtual fabs should be physically based; *i.e.*, they should use and solve equations which represent the physical phenomena which occur in the processes simulated, to the degree that the phenomena are understood. Early topography simulators were not based upon the physics which occur; *e.g.*, users specified the directionality of a deposition process. A physically based simulator predicts the profile evolution, including directionality, using information on the operating conditions and physics involved in the process.

One major barrier to the development of useful topography simulation packages for virtual fabs has been the lack of robust topography evolution algorithms (and codes). Algorithms for the evolution of fully three dimensional (3d) surfaces are appropriate for

# DEPOSITION OF AMORPHOUS SILICON

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## 1. Introduction

In 1969 Chittick *et al* [1] discovered that hydrogenated amorphous silicon (a-Si:H) deposited from  $\text{SiH}_4$  glow discharges is a semiconductor, and in 1975 Spear and LeComber [2] demonstrated that a-Si:H could be doped by adding  $\text{B}_2\text{H}_6$ ,  $\text{AsH}_3$  or  $\text{PH}_3$  to  $\text{SiH}_4$ . This opened the possibility of making thin-film devices at low temperature ( $100\text{-}300^\circ\text{C}$ ) on glass substrates for various applications : photovoltaic solar cells, xerography, vidicon tubes, optical sensors, light emitting diodes and thin-film transistors (TFT) for scanners and active-matrix liquid-crystal displays (AM-LCD) [3]. A large effort of basic and applied research accompanying industrial developments has been spent to study deposition processes and properties of a-Si:H and related alloys (a-SiC<sub>x</sub>:H and a-SiGe<sub>x</sub>:H), and microcrystalline silicon ( $\mu\text{c-Si:H}$ ). Simultaneously many techniques alternative to plasma-enhanced chemical vapour deposition (PECVD) were explored : photo-CVD using UV or IR photolysis of  $\text{SiH}_4$ , hot-wire-CVD using the pyrolysis of  $\text{SiH}_4$  on a tungsten filament as a source of reactive species, sputtering or evaporation of Si in the presence of  $\text{H}_2$ , etc... Other molecules such as  $\text{Si}_2\text{H}_6$  or  $\text{SiF}_4$  were also used [4]. All these approaches provide materials with analogous if not identical properties. Nevertheless PECVD in radio-frequency (RF) parallel-plate discharges is still preferred for large area industrial deposition.

We first present the structural and electronic properties of a-Si:H to point out key issues in the optimization of PECVD. Secondly from a survey of the  $\text{SiH}_4$  plasma physico-chemistry we indicate what are the main reactive species (radicals and ions), the various power dissipation mechanisms in  $\text{SiH}_4$  discharges and the conditions leading to homogeneous nucleation of particles (powder formation). Then we show how the surface reactivity of radicals, the ion energy, and other ingredients govern the final film properties.

## 2. Basic properties of a-Si:H

### 2.1. STRUCTURE, H BONDING AND MICROSTRUCTURE

From X-ray diffraction of a-Si and a-Si:H films it appears that the distances of the first and second Si nearest neighbours, hence the tetrahedral coordination of Si is preserved. But the broadening of the peaks in the correlation function indicates slight distortions in bond lengths and bond angles which destroys the long-range periodicity of the network

## HIGH DENSITY SOURCES FOR PLASMA ETCHING

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### 1. Introduction

There is great current activity in the development of high density sources for plasma processing of microelectronic devices. Much of the interest has been stimulated by the need to control and reduce plasma-induced device damage. Plasma sheath potentials in capacitively coupled parallel plate reactors can range from hundreds to thousands of volts. Plasma ions falling through these potentials can cause unacceptably high device damage, such as atomic displacement and gate oxide damage, leading to threshold voltage shifts and gate leakage. In parallel plate discharges, the roles of plasma generation and wafer biasing are coupled: higher input power (to increase the plasma density) will simultaneously increase the sheath self-bias potential.<sup>1</sup> There is thus a critical need for high density sources in which the roles of plasma generation and substrate biasing are decoupled, so that high plasma densities can be combined with low ion energies. For example, a set of plasma objectives for anisotropic low damage etching would be:

- Low operating pressure: 1 - 10 mTorr;
- High plasma ion concentrations:  $> 10^{11} \text{ cm}^{-3}$ ;
- High ion flux to the wafer:  $> 10 \text{ mA/cm}^2$ ;
- Controllable low ion energy:  $< 30 \text{ eV}$ ,

with a sharp, nearly monoenergetic energy distribution and decoupled ion flux density and ion energy.

Table 1 compares the parameters of radio frequency (rf) driven parallel plate diode and a typical high density plasma. Note that while the ion energy may be 10 to 100 times lower in the high density discharge, the ion power flux to the wafer,  $J \cdot V_s$ , is comparable in both cases.

In the following sections, we first briefly discuss methods of plasma production, including the rf capacitively coupled diode. We will then discuss inductively coupled plasma sources, both nonresonant and resonant (the helical resonator), and wave driven sources (electron cyclotron resonance and helicon mode launchers). The goal is to treat succinctly those high density sources which are actively being evaluated for wafer processing. Longer discussions can be found in the literature.<sup>2,3</sup> A brief discussion will be given of multipolar plasma confinement, as it is often used with decoupled high

## RESONANT PLASMA EXCITATION BY ELECTRON CYCLOTRON WAVES - FUNDAMENTALS AND APPLICATIONS

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### 1. Introduction

In contrast to capacitively coupled radio frequency glow discharges, inductively excited low pressure plasmas play only a minor role in recent plasma based surface and thin film technologies as applied for semiconductor processing or the production of microelectronic devices. This is mainly a consequence of the high lateral homogeneity in parallel plate reactors which is favorable for uniform processing of large area plane substrates. On the other hand, inductively coupled plasmas have the advantage that no plasma exciting electrodes have to be inserted into the plasma chamber. Thus, a geometrically simply shaped vessel can be filled with plasma, and any electrode inside the chamber is introduced intentionally for the desired surface modification or deposition process. The usual „ring“ discharges, in which the plasma acts in principle as a single turn secondary coil of an r.f. transformer with a multiturn primary coil surrounding the plasma vessel, suffer in general from a radially inhomogeneous plasma structure. In addition, the relatively high r.f. voltage between the ends of a multiturn exciting coil causes the superposition of a secondary capacitive discharge. Other restrictions result from the limitations for an upscaling of the diameter of the discharge vessel.

The present chapter deals with an approach which enables on one hand to utilize the clear advantages of an inductively excited low pressure plasma, namely the possibility to keep a simply configured plasma vessel free of internal electrodes. It will be shown that, on the other hand, the disadvantages of a simple ring discharge will be avoided, and that high density low pressure plasmas with a smooth variation of the plasma parameters are achieved. In such a system plasma excitation is established through an electrodynamic effect by which a standing wave of a propagating electromagnetic mode, the so-called electron cyclotron waves, is matched to the dimensions of the plasma container. This „electron cyclotron wave resonance“ ECWR has to be well distinguished from the

## The Transition from Capacitive to Inductive to Wave Sustained Discharges.

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### Abstract.

Plasma sources used in the processing of thin films can be divided into three distinct categories, capacitive (E), inductive (H) and wave (W) sustained discharges. The simple parallel plate system is typical of E discharges where the plasma is sustained by the RF electric field of the powered electrode upon which the substrate is situated. H mode discharges are sustained by currents induced in the plasma by currents flowing in an antenna external to the plasma. In the W mode, the antenna currents excite a propagating wave in the plasma which interacts with the plasma electrons and heats them. The H and W modes can be regarded as remote excitation as the electrode or antenna need not be in contact with the plasma allowing an independent bias (E mode) to be applied to the substrate. This paper will describe the basic physics of each of these discharges and will show in which parameter regions each is dominant.

### The Parallel Plate (E) Discharge.

This is the classic embodiment of the Reactive Ion Etching (RIE) reactor, whE.electronics industry since the mid 1970's. RF power, generally at 13.56 MHz, is fed to a plate in a vacuum vessel via an LC network that matches the 50 ohm RF generator output to the plasma impedance. Since the earthed walls of the vacuum vessel normally have an area about ten times greater than the powered electrode, this is called an asymmetric discharge. The average voltage difference between the plasma and the walls and the plasma and the powered electrode is determined by the reactances of the corresponding sheaths which depend on the sheath capacitances. Clearly, both the area of the sheaths, which is determined by the reactor geometry, and the thickness of the sheaths, which is determined by the plasma density and voltage difference, will play a role in the sheath capacitances. For the voltage division between the plasma and the powered electrode ( $V_1$  with area  $A_1$ ) and the plasma and the earthed electrode ( $V_2$  with area  $A_2$ ) we can write:

$$\frac{V_1}{V_2} = \frac{Z_1}{Z_2} = \frac{C_2}{C_1} = \frac{S_1 A_2}{A_1 S_2} = \frac{A_2}{A_1} \left[ \frac{V_1}{V_2} \right]^{\frac{3}{4}} \left[ \frac{n_2}{n_1} \right]^{\frac{1}{2}} \quad 1)$$

where we have used the Child-Langmuir relation for the sheath and assumed a spatially uniform electron temperature ( $T_e$ ) (see section 11.4 of ref. 1)

If the plasma density were spatially uniform the voltage ratio would scale as the fourth power of the area ratio. Experimentally, the scaling power is less than 2.5, due to non uniform plasma density. Taking a more realistic view of the plasma, the most common ionization mechanisms are electron acceleration due to sheath heating and ion induced secondaries being accelerated by the sheath on the powered electrode. Both these mechanisms are most effective close to the powered electrode so we can consider the plasma to be created in this region. In the most simple view, half of the plasma will diffuse toward the powered electrode and the other half toward the earthed surfaces. Experimental measurements show that the diffusion (without recombination) in a typical asymmetric system where the ionization is close to the powered electrode is essentially spherical conserving flux, even in the presence of an earthed counter

## PHYSICS OF SURFACE-WAVE DISCHARGES

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### 1. Surface-Wave Sustained Discharges: Short History and Present Situation of Development

The existence of electromagnetic waves guided by a plasma-dielectric structure was disclosed by Trivelpiece and Gould in 1959 [1]. Initially designated as space charge waves, then as Trivelpiece-Gould modes, they are now more widely known as (electromagnetic) surface waves (SW). In the sixties, many articles were devoted to the study of such waves (see e.g. [2],[3],[4],[5],[6]). First used as a diagnostic means of the electron density in positive column plasmas, it was realized in the seventies that these waves could be employed to generate long electrodeless plasma columns. Tuma [7] was the first to show such a possibility; trying to achieve a plasma within a resonant cavity, he actually observed that plasma was extending outside it and that it was sustained by a travelling wave which he identified as a surface wave. Following the design and development of efficient surface wave launchers [8], the systematic investigation of such discharges started at the end of the seventies. Nonetheless it is really in the eighties that SW discharges proved their remarkable potential for modelling high frequency plasmas in general [9] and also for applications [10]. Then, at the beginning of the nineties, it was proposed that SW be utilized to generate magnetoplasmas under broader operating conditions than common ECR discharges [11].

A great deal of the success of SW plasmas results from their extraordinary flexibility in terms of operating conditions, which include dimensions of the discharge vessel, nature and pressure of the gas, wave frequency and, eventually, magnetic field intensity. These discharges can be produced efficiently at frequencies ranging from approximately 10 MHz to 10 GHz; operation down to 200 kHz has been achieved but impaired due to the lack of an adequate impedance matching circuit. The gas pressure that can be used ranges from the sub-millitorr domain up to several times atmospheric pressure. Discharge tube



## **SURFACE SCIENCE ASPECTS OF ETCHING AND WALL REACTIONS IN HIGH DENSITY PLASMAS**

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### **1. Introduction**

Within the last ten years or so, in response to the needs of the semiconductor processing industry, new plasma etching machines involving high density plasmas ( $>10^{11} \text{ cm}^{-3}$ ) have been developed. The requirement that lead to this change from low density plasmas, ( $<10^{11} \text{ cm}^{-3}$ ), to high density plasmas was a need for lower energy ion bombardment of the wafer (often  $<100 \text{ eV}$ ). In reactive ion etching (RIE) with low density plasmas, ion energies of several hundreds of eV are usually incident on the wafer and the damage and selectivity loss caused by these ions was found to be unacceptable in some critical applications. However decreasing the ion energy also decreases the etch yield per ion and therefore, in order to maintain the etch rates, high ion fluxes are required. Hence the need for high density plasmas. Furthermore, low pressure operation ( $<10 \text{ millitorr}$ ) is often needed to achieve the desired profile shape in the etched feature.

### **2. Etching Reactions**

#### **2.1 IONS AS A SOURCE OF CHEMICAL SPECIES**

In RIE with low density plasmas, it is clear that the chemical species must be provided by the neutral atoms, radicals or molecules. The chemical flux provided by the low ion flux ( $<0.5 \text{ ma/cm}^2$ ) does not deliver enough chemical species to the surface to sustain the observed etch rates.

However the situation changes when one considers high density plasmas where the ion current density can be  $10\text{-}20 \text{ ma/cm}^2$ . For example, if the etch rate of Si in a chlorine plasma is  $300 \text{ nm/min}$  and the ion current density is  $20 \text{ ma/cm}^2$ , the etch yield is only  $0.2 \text{ Si atoms/ion}$ . If the incident ion is  $\text{Cl}^+$  and if the etch product is  $\text{SiCl}_2$ , then the chemical requirement is  $0.4 \text{ Cl atoms per incident ion}$  which obviously can be provided by the ion itself.

## PLASMA-SURFACE INTERACTIONS

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### 1. Introduction.

Low Pressure Plasma (LPP) processes are non-equilibrium surface modification techniques that allow the modification of solid substrates by means of:

- a - the deposition of void-free, well adherent thin films (100 - 10,000 Å) of chemical composition and properties tuneable *in continuo* with the plasma parameters (Plasma Enhanced - Chemical Vapour Deposition, PE-CVD);
- b - the modification of the very first surface layers of solid materials by grafting chemical functionalities (Plasma Treatments, PT);
- c - the ablation of materials through reactions with active species generated in the plasma to form volatile products (Plasma Etching).

LPPs are currently generated in laboratory and industrial scale by applying a direct or an alternated (KHz, MHz or GHz) electric field to a flowing gas mixture confined in a properly configured low-pressure reactor. Radio Frequency (RF) fields at 13.56 MHz are currently more widely utilised.

It worths to remind soon that PE-CVD and PT are important technologies which allow to design an *entirely novel class of materials*, generally in the form of thin films, with unique characteristics and only a few, or even no, correlations with conventional massive materials [1]. The principal features of LPP processes in the field of thin film technology are:

- 1- the possibility of continuously varying the chemical composition of treated surfaces and, obviously, their physical and chemical properties in a very broad range. Properties which can be tuned include wettability, adhesivity and dyeability, refractive index, hardness, barrier characteristics, chemical inertness, biocompatibility, etc.;
- 2- the possibility of controlling the process by means of *in situ* plasma diagnostics and obtaining fully controlled, reliable and reproducible processes;
- 3- the feasibility of scaling up reactors to production needs and to obtain fast and homogeneous processes;

## **Cl<sub>2</sub> PLASMA - Si SURFACE INTERACTIONS IN PLASMA ETCHING:**

*X-ray Photoelectron Spectroscopy After Etching, and Optical and Mass Spectrometry  
Methods During Etching*

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### **ABSTRACT**

The interaction of a chlorine plasma with a Si(100) surface has been investigated by angle resolved x-ray photoelectron spectroscopy (XPS), laser-induced thermal desorption with laser-induced fluorescence detection (LD-LIF), optical emission, and mass spectrometry. From XPS, it was found that the amount of chlorine incorporated at the Si surface increases with ion energy, and doesn't change with long exposure to the plasma. Chlorine is present solely as SiCl<sub>x</sub> (x = 1-3) with average relative coverages of [SiCl] : [SiCl<sub>2</sub>] : [SiCl<sub>3</sub>] ≅ 1 : 0.33 : 0.1. These coverages don't depend strongly on ion energy between ~50 and 300 eV. Moreover, there is a substantial amount of disordered Si within the chlorinated layer at high ion energy, reflected in a broadening of the 99.4 eV Si peak and the appearance of a shoulder at 98.8 eV, ascribed to Si with a dangling bond. From modeling of the angle-resolved signal intensities of the Si-chloride species as a function of the XPS take-off angle, thicknesses of 20-35 Å and 6-10 Å were derived for the SiCl<sub>x</sub> layer at bias voltages of -240 and 0 VDC, respectively. The total Cl content of these layers increased from 1.6x10<sup>13</sup> Cl/cm<sup>2</sup> at 0V to 3.0x10<sup>13</sup> Cl/cm<sup>2</sup> at -240 VDC bias. This shows that the top surface layer is predominantly SiCl<sub>2</sub> and SiCl<sub>3</sub>, while just below the surface, mainly disordered Si and SiCl are present. Laser-induced thermal desorption was used to measure Cl-coverage in real time. These measurements, in addition to real time ellipsometry measurements, showed that the layer present during etching is stable when the plasma is extinguished and the gas pumped away. The laser-desorption measurements, in conjunction with optical emission actinometry

## **PARTICLE IN CELL MONTE CARLO COLLISION CODES(PIC-MCC); METHODS AND APPLICATIONS TO PLASMA PROCESSING**

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### **Abstract**

Simulations complement analytic modeling and lab experiments, following electron, ion and neutral motion in discharges used for processing materials, especially semiconductors. Simulations are shown of charged particle motion, fields, potentials, densities, and energies, etc., in the plasma volume and at surfaces. The PIC-MCC methods displayed come from first principles, fully nonlinear, run on fast workstations or PC's, with many (non-invasive) diagnostics, with 1d, 2d, and 3d models, all with 3 velocity components. Examples are given, with experimental verification. Comparison is made between fluid and particle methods. The codes displayed are free.

### **1. Introduction to Particle Simulations**

Our objective is to answer the question: What can particle simulations tell us about plasmas with relevance to processing?

In order to answer this question, we will first tell what particle simulation is and how to do particle simulations, with some examples. Then, we will follow with some examples and include some comparisons with laboratory experiments, in order to gain confidence with our simulation methods.

In general there are two kinds of plasma simulations.

One kind is using a fluid model, numerically solving the plasma fluid equations with boundary conditions, for the fluid density, drift velocity, and temperature, as a function of time and space. This approach is very popular, using the fluid equations found in all plasma texts. Usually the solutions are for  $n$ ,  $v$  and  $T$  of the ions and electrons, the first three moments of the distribution functions. The electron and ion distribution functions,  $f(x,v,t)$  and  $F(x,v,t)$ , are assumed to be Maxwellian. Typical simulations for processing may run for a few hours on a medium fast workstation.

Another kind is using a many-particle model, with a sufficiently large number of particles to generate relatively smooth distribution functions,  $f$  and  $F$ , everywhere needed. With fast PC's and workstations, one can "push" a million particles per second in 1 and 2 dimensions, say, 20,000 particles advanced 50 time steps. The solutions are

# FLUID AND HYBRID MODELS OF NON EQUILIBRIUM DISCHARGES

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## I. Introduction

In this paper we present a general discussion of fluid and hybrid models of non equilibrium discharge plasmas. We emphasize in particular the description of the charge particle - electric field submodel and do not consider the questions of plasma chemistry and plasma surface interaction. Assumptions implied by the fluid description, and some aspects of the numerical methods are discussed.

We describe the different categories of fluid and hybrid models in section II. In section III, we define the different time scales which characterize non equilibrium low temperature plasmas. Some of the assumptions used in fluid models are discussed in section IV. Section V presents a few aspects of the numerical methods. Some examples of 2D discharge models are discussed in section VI.

## 2. Fluid and hybrid models

### 2.1. SELF-CONSISTENT FLUID AND HYBRID MODELS

*Fluid Models.* Particle-In-Cell Monte Carlo Collision models (PIC MCC) [1] provide a complete description of charged particle transport in weakly ionized plasmas since space and time variations of electron and ion distribution functions can be deduced from these models. Physical processes such as collisionless or stochastic heating are very well described by PIC MCC models and are more difficult to account for in "more macroscopic" models.

However, the degree of detail available from PIC MCC models is not always necessary, and can be computationally very expensive. For example, when collisional electron heating (ohmic heating) is dominant, i.e. when electron heating can be accurately described by  $J_e \cdot E$  with  $J_e = \sigma_e E$  (where  $J_e$  is the electron current density,  $E$  the

## OPTICAL DIAGNOSTICS OF PROCESSING PLASMAS

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Optical interactions with the plasma provide powerful probes for monitoring the operation of semiconductor processing reactors. The probes do not perturb the system under study, and can be applied *in situ* to provide real-time information. This section provides a brief review of the physics involved with these diagnostic probes, followed by brief descriptions of several of the more popular methods. Length limitations restrict severely the level of coverage, and several important techniques are not discussed at all. It is hoped that sufficient information is available that the interested reader will be able to find a more complete treatment of any subjects of interest.

### 1. Energy Levels of Atoms and Molecules

Light interacts with species in the plasma by causing transitions between energy levels of the species coupled with the emission or absorption of a photon of energy just equal to the energy separation of the levels involved. Thus the spectrum of light emitted or absorbed by a plasma reflects the spectrum of energy levels of the species in the plasma. Because the energy level spectrum of each species is unique, analysis of the electromagnetic spectrum provides a means for identifying the species present. Further, the intensity of the emission or absorption provides information about species density, and state of excitation of each species.

#### 1.1 ATOMIC ENERGY LEVELS

Consider first a one-electron atom such as H, or  $\text{He}^+$ , or  $\text{Li}^{++}$ , etc. Neglecting spin-orbit and other smaller interactions, there are five good quantum numbers:  $n$ ,  $l$ ,  $s$ ,  $m_l$ , and  $m_s$ . Because of the spherical symmetry, the energy of a given level should not depend on  $m_l$  or  $m_s$ . Further  $s = \frac{1}{2}$  always since there is only one electron. Thus we would expect the energy of a level to depend on  $n$ , and  $l$ . For the case of a Coulomb potential, however, it happens that the dependence on  $l$  drops out also, and

$$E_{n,l,s,m_l,m_s} = -Z^2 \frac{E_0}{n^2} \quad (1)$$

where  $E_0 = 13.595 \text{ eV} = 109678.764 \text{ cm}^{-1}$ , and  $Z$  is the number of protons in the atom nucleus. Empirical data verify the validity of Eq. (1). The spin-orbit interaction splits

## OPTICAL DIAGNOSTICS OF PLASMAS: A TOOL FOR PROCESS CONTROL

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### 1. Introduction

Low pressure glow discharges are widely used in new technologies and particularly for materials surface processing as : etching, deposition of thin films and surface passivation. In particular, plasma processing has had the largest impact in silicon integrated circuit technology by making it possible to etch submicron sized features with vertical side walls in silicon, metals, insulators and resists [1]. However, to meet the requirements of material properties and the performances of sophisticated device structures, it is necessary to control precisely the reproducibility of rather complex plasma processes. This precise control can be achieved by in-situ diagnostics in the plasma gas-phase or at the surface of the material under process. On the other hand, empirical optimization of plasma parameters (gas composition and density, r.f. power, reactor geometry, etc...) has produced many successful process "recipes". However, with new in-situ diagnostic techniques and computer modeling, it is now possible to obtain detailed information on the chemistry and physics of these processing plasmas, and their interaction with surfaces.

Optical diagnostics are particularly well-suited for in-situ plasma diagnostic studies because they are non-intrusive, species-selective, and yield information with good space and time resolution. They are based on the interaction of the atomic and molecular species present inside the plasma with electromagnetic radiation. Optical diagnostic methods can be classified into two categories :

- i) "passive" techniques, where plasma emission, often spectrally resolved, gives information on species in their electronically excited states. Since, in general, these excited species are produced by electron impact excitation of atoms (or molecules), their relative emission intensities provide information about the species present inside the plasma.
- ii) "active" techniques in which an external light source (laser or spectral lamp) is used to probe the plasma or the processed surface. In this case, information about the interacting species are deduced from the absorption or the induced fluorescence signals.

In this paper, several diagnostic techniques, based on optical spectroscopy, will be presented. Some of these techniques are currently used for in-situ process control in industrial equipment, *i.e.* : endpoint detection and actinometry. Some others, such

## INFRARED ABSORPTION SPECTROSCOPY AS A DIAGNOSTIC FOR PROCESSING PLASMAS

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### 1. Introduction

Infrared spectroscopy is a technique which so far has not very frequently been used for the diagnostics of processing plasmas. There are a number of reasons for this. Firstly the technique is rather difficult to implement. Infrared light can not be seen, and therefore the alignment of the optics is rather difficult. Typically the equipment which is needed is rather expensive. On the other hand, infrared absorption spectroscopy is able to generate very accurate and detailed data. In table 1 the technique is compared with various other popular optical diagnostics.

Table 1: comparison of various popular diagnostic techniques

	Emission spectroscopy	UV-visible absorption	IR absorption	LIF	Raman and CARS
Expense	cheap	cheap	high	very high	very high
Implementability	simple	average	average	difficult	difficult
Ground state detection	no	no	yes	yes	yes
Absolute densities	no	yes	yes	yes	yes
Spatial resolution	average	average	average	good	good
Sensitivity	good	very good	good	very good	poor

In general, infrared spectroscopy will be used for the determination of the chemical composition of the plasma. Molecules as well as radicals can be detected. The technique is non-intrusive; the plasma is not disturbed at all.

In this paper, we will first summarize the theoretical analysis of infrared absorption band shapes. Then we will treat the instrumentation. We will conclude by showing some examples of the interpretation of measurement results.



## ELLIPSOMETRIC ANALYSIS OF PLASMA DEPOSITED AND PLASMA ETCHED MATERIALS

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### 1. Introduction:

This paper is an introduction and overview of spectroscopic ellipsometric analysis of thin films, with special emphasis on plasma deposited and plasma etched materials. The intent is to illustrate the power of this recently enhanced technique for *ex-situ* post-process, and *in-situ* real-time microstructural analysis, and to discuss some issues not normally presented in papers.

Materials analysis capability by ellipsometry has been enhanced enormously in recent years because of advances in personal computers and the switch from single wavelength (or a few) to spectroscopic ellipsometry. None of the materials problems examples discussed in this paper can be solved using single-wavelength ellipsometry. Single wavelength ellipsometry is used only in those situations for which the material structure and composition are extremely well known and not complex.<sup>1</sup> In contrast, spectroscopic ellipsometers offer excellent materials analysis capability and a high confidence level in experimental results that make it a valuable diagnostics tool.<sup>2-7</sup>

### 2. Experimental:

The basic concepts of ellipsometry are illustrated in Figure 1.<sup>2,8</sup> An incoming light beam of known polarization state encounters a material under study, and the polarization state of the outgoing light is analyzed. Measurements can be made with the transmitted or reflected light, or both, but normally the reflected beam is used.

There are several optical configurations for defining and measuring the beam polarization state. The most common are based on either rotating polarizer, rotating analyzer, or modulated retardance.<sup>8,9</sup> Figure 2 shows the layout for a rotating analyzer ellipsometer consisting of an arc lamp to provide a spectral continuum of black-body radiation that is dispersed by a monochromator

# MASS SPECTROMETRY OF REACTIVE PLASMAS

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## 1. Introduction

The first "mass spectrographs" were invented by Aston and Dempster in 1918-1919 in order to separate isotopes of various ions. These apparatuses were based on a magnetic field dispersion and rather complicated and heavy to use. Since then, with the development of modern ion optics [1], the improvement in vacuum technology and detectors and eventually the invention of the compact quadrupole mass filter [2], mass spectrometers have become routinely used in many fields of experimental physics and chemistry [3,4].

As opposed to optical UV-visible and IR diagnostics depending on accessible electronic or vibrational excited states of a few atoms and simple molecules, mass spectrometry can detect, in principle, all the charged and neutral species coming from a plasma. This made the technique very attractive for *in-situ* characterization of reactive plasma processing, in particular in plasma-enhanced chemical vapor deposition (PECVD) and plasma etching (PE) or reactive ion etching (RIE) [5-7]. Another common application is the *ex-situ* surface chemical analysis by secondary ion mass spectroscopy (SIMS). Here we review the basic principles and technical aspects of different mass spectrometers with more emphasis on the quadrupole mass spectrometer (QMS) which is by far the most widely used. Then we examine the applications of mass spectrometry from the simplest to the most sophisticated diagnostics. Starting with gas analysis (partial pressure measurements), we turn to the characterization of the positive and negative ion flux and energy distribution. Finally we show how appearance potential mass spectrometry can be used to determine atom and radical densities near the walls. We do not cover the wide applications of SIMS although this technique is classically used for chemical profiling of semiconductor materials after deposition of etching.

## 2. Principles and technical aspects of mass spectrometers

Mass spectrometers such as those represented in Figures 1 and 2 involve several components: an ion source (plasma or ionization chamber), a system of ion optics, an energy analyzer, a mass filter (usually a quadrupole) and finally a detector. The ionisation chamber for neutral gas analysis or the extraction of plasma ions are considered in § 3 and 4. Here we examine the other components. In the following ions are characterized by their mass  $m$ , their kinetic energy  $\mathcal{E}$  and their charge  $Ze$ ; this applies as well to positive ions (cations,  $Z \geq 1$ ) and negative ions (anions,  $Z \leq -1$ ).

# DEPOSITION OF SILICON DIOXIDE FILMS USING THE HELICON DIFFUSION REACTOR FOR INTEGRATED OPTICS APPLICATIONS.

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## Abstract.

Existing optical fibre and fibre-device fabrication techniques have been complemented recently by the development of new processes for the fabrication of planar optical waveguides and devices. These processes rely on new forms of plasma reactors and diagnostic systems which allow in-situ control of optical parameters such as refractive index. These plasma processing systems allow the fabrication of optical devices which are not readily feasible in fibre technology, and allow the fabrication of very compact and highly complex optical circuitry which can be produced on a single photonic chip. They also offer the potential to integrate photonic devices with semiconductor sources and detectors to realise a compact, hybrid photonic-optoelectronic chip, complete with fibre pig-tailing. Because of their compactness and potential low cost, these types of photonic chips are attractive components for future high-capacity optical telecommunications and other networks now being planned as part of the information super highway. The paper presents the physical constraints and design rules for the fabrication of the devices, and the research carried out using a helicon plasma reactor to grow the thick films of silica necessary for the waveguides. From the start, the reactor was designed to process substrates at low temperatures to allow the integration with other optical and electronic components on the same wafer. Hence a considerable amount of research was carried out on the relation between the plasma parameters and the physical properties of the films deposited. The last section of the paper describes the fabrication of an actual device; a 1:8 splitter, and its characteristics.

## REMOTE PLASMA PROCESSING

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### 1 Introduction

Direct exposure of microelectronic devices and circuits to processing plasmas can degrade the performance of these components by charging damage, ion impact damage and defects introduced by ultraviolet photons. Charging damage is due to the existence of an excess potential across the  $\text{SiO}_2$ , which leads to tunneling of electrons through the oxide which introduces permanent defect states in the  $\text{SiO}_2$  and degrades its reliability.[1] Ion impact damage can lead to bond breaking and atomic displacement and/or impurity mixing in the surface region of the exposed materials.[2] In addition, it lowers the etch selectivity that can be achieved in the process which may not be acceptable for non-critical applications, e.g. mask stripping. A third type of damage is due to the high flux of energetic photons that irradiates the substrate in a direct plasma process. The photon flux from the plasma produces traps in insulators and interface states at insulator/semiconductor interfaces which degrade the device performance.[3]

These problems have stimulated a strong interest in charge-free processing methods. The most important of these are a) downstream plasma etching and chemical vapor deposition, b) energetic neutral beam processing, or c) techniques not involving plasmas, e.g. photon-based processing, of which an important example is ultraviolet (UV) assisted resist stripping. A discussion of a) and b) is presented in this article.

### 2 Chemical Downstream Etching (CDE)

Chemical downstream etching (CDE), also sometimes called chemical dry etching, is extensively used in the semiconductor industry for etch applications not requiring etch directionality.[4-6] These include stripping of masking layers, surface cleaning and surface modifications. In CDE the substrate is located outside of the plasma region. Long-lived radicals and excited states diffuse from the plasma zone to the substrate. Additional gases may be injected downstream from the plasma which will mix with the plasma-produced energetic species and produce precursors of etching or growth reactions. The ideal CDE reaction is a spontaneous chemical reaction, which does not require ion, electron or photon bombardment. Spontaneous etching reactions have the characteristic that they occur also at non-line-of-sight surfaces which is important for cleaning applications. The strong dependence of the etch rate on intrinsic surface reactivity without ion-induced sputtering

## DUSTY PLASMAS: FUNDAMENTAL ASPECTS AND INDUSTRIAL APPLICATIONS

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### 1. Introduction

Dusty plasmas have recently acquired a lot of attention. The subject was initiated by the semiconductor industry. With the arrival of VLSI and ULSI (very/ultra large scale integration) plasma etching and plasma deposition techniques have become indispensable. With the decreasing feature sizes on the devices the tolerance for dust particles becomes smaller. Now that feature sizes are below 0.25 micron, very small dust particles with a diameter of only a few tenths of a micron can kill the device. Therefore about 5 years ago substantial research efforts were started in order to investigate the trapping and transport of dust particles in processing plasmas.

The amorphous silicon community joined in a few years later. Several groups observed that silicon dust readily grows in glow discharges in silane. Also in this field the research initially focused on getting rid of the dust. A few years ago the focus changed. Now several groups investigate the possibilities which are opened by the presence of dust in the plasma.

In this paper we will give an outline of the dusty plasma research. Results obtained in many groups from all over the world are combined.

#### 1.1. FORCES ON THE PARTICLES

Several forces work on the particles.

- *The electrical force.* The mobility of electrons is larger than the mobility of positive ions. This phenomenon causes dust particles to charge up negatively. Since all particles have a negative charge, they will repel each other. In general the plasma glow is surrounded by a space charge region. In this region there is an electrostatic field directed towards the electrodes and chamber wall. This electrostatic field also traps the negatively charged dust particles in the plasma glow.

## LOW ENERGY PLASMA BEAMS FOR SEMICONDUCTOR TECHNOLOGY

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### 1. Introduction

The application of broad low energy ion beams in recent surface and thin film technology [1-4] is often superior to plasma based processing where the respective surface or thin film structure is in direct contact with the bulk of a low pressure discharge. This is mainly due to the directionality, but even more to the high flexibility of ion beams with respect to their energy and composition. Thus, the versatility for the generation of thin films with specific properties can be decisively expanded in comparison to „random“ processes as evaporation or sputtering by the accurate control of the kinetic properties or the angle of incidence of the arriving species. Well collimated, low energy beams of inert or reactive ions may sometimes prove as a better means for mask assisted etching particularly in the sub-micron regime than ion extraction through a thin plasma edge sheath which is influenced by the changing contours of the developing structure.

Apart from the higher experimental expenditure the transported electrical charge may often become a serious obstacle for the application of an ion beam, especially in the low energy regime. The present chapter is intended to show that such disadvantages are avoided with recently developed plasma beam sources consisting of a monoenergetic ion component and co-traveling charge compensating electrons. After a short discussion of the fundamental differences between low energy ion and plasma beams, an r.f. method for the co-extraction of ions and electrons from a low pressure plasma for the production of monoenergetic electrically neutral plasma beams will be elucidated. Subsequently, the construction and the operation of low energy plasma beam sources, and the beam properties will be described. The examples for the application of low energy plasma beams comprise the formation of nitride and diamond-like carbon layers, and inert or reactive plasma beam etching for surface conditioning or microstructuring.

## PROCESS CONTROL CONCEPTS

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### ABSTRACT

To follow the historical trend of 30%/function per year reduction in cost of integrated circuits and to meet the future processing challenges, semiconductor processing equipment must include improved control systems and semiconductor manufacturers must deploy more advanced control techniques. An understanding of basic control concepts is necessary before discussing these control system improvements and their applications. To furnish this understanding, this paper provides a definition of Advanced Process Control. An overview of relevant control terminology, attributes, and implementation forms are presented. Issues such as requirements, specification of good control, deadtime, and stability are also included. The technical and financial reasons for control are also introduced. The relationship between the various concepts are highlighted.

### 1. Introduction

The Semiconductor Industry Association produces a Roadmap for the industry's technology and processing needs for the future. The most recent version of the Roadmap stresses the need for productivity improvement in order to maintain the industry's historical 30%/function per year reduction in cost [1]. The items utilized in the past to achieve this cost reduction are no longer readily available, such as yield

## ISSUES AND SOLUTIONS FOR APPLYING PROCESS CONTROL TO SEMICONDUCTOR MANUFACTURING

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### ABSTRACT

To follow the historical trend of 30%/function per year reduction in cost of integrated circuits and to meet the future processing challenges, semiconductor processing equipment must include improved control systems and semiconductor manufacturers must deploy more advanced control techniques. In this paper, the challenges of applying process control to semiconductor processing will be examined. Specifically, the various sources of variation which need controlling and diagnosing will be presented. The variation due to physical process changes will be introduced first, and their dynamics will be clarified. Current control practices and metrology limitations will then be reviewed, and the issues for achieving tight control that these practices and limitations generate will be highlighted. The paper will conclude with some examples of and suggestions for successful application of process control.

### 1. Introduction

The Semiconductor Industry Association produces a Roadmap for the industry's technology and processing needs for the future. The most recent version of the Roadmap stresses the need for productivity improvement in order to maintain the industry's historical 30%/function per year reduction in cost [1]. The items utilized in the past to achieve this cost reduction are no longer readily available, such as yield